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Polarity-dependent resistance switching in GeSbTe phase-change thin films: The importance of excess Sb in filament formation

Ramanathaswamy Pandian,[1,2] Bart J. Kooi,[1,a)] Jasper L. M. Oosthoek,[1] Pim van den Dool,[1] George Palasantzas,[1] and Andrew Pauza[3]
[1]*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2]*Institute of Electronic Materials, Institute of Solid State Research (IFF), Research Centre Juelich, 52428 Juelich, Germany*
[3]*Plarion Ltd., Melbourn Science Park, Melbourn, Hertfordshire SG8 6HB, United Kingdom*

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We show that polarity-dependent resistance switching in GeSbTe thin films depends strongly on Sb composition by comparing current-voltage characteristics in Sb-excess $Ge_2Sb_{2+x}Te_5$ and stoichiometric $Ge_2Sb_2Te_5$ samples. This type of switching in $Ge_2Sb_{2+x}Te_5$ films is reversible with both continuous and pulsed dc voltages less than 1.5 V. Low and high resistance states of this switching can be attributed to formation and rupture, respectively, of electrically conductive Sb-bridges between the $Ge_2Sb_2Te_5$ crystals and electrodes through the resistive amorphous phase. The coexistence of polarity-dependent resistance switching with amorphous-crystalline phase-changes renders great opportunities to expand the applicability of GeSbTe films for data storage applications. © *2009 American Institute of Physics*. [doi:10.1063/1.3276272]

Chalcogenide materials have been more than a shining success as phase-change materials in rewritable optical recording known from the compact disk, digital versatile disk, and Blu-ray disk formats.[1–5] Currently, they are also under intense investigation for application in a nonvolatile phase-change random access memory.[6–15] Apart from the amorphous-crystalline phase change, certain compositions of chalcogenide materials show another resistance switching mechanism which is activated by the polarity (directionality) of the applied electric field.[16–24] Although, the exact physical mechanism underlying this polarity-dependent resistance (PDR) switching is still under strong debate, it is commonly attributed to the solid-state electrolytic character and high ionic conductivities of these materials.[25]

Recently, we demonstrated that in a single material, derived from the GeSbTe (GST) ternary alloy system, both switching mechanisms (phase-change and PDR) were possible.[26,27] Although GST has been a prototype material system for phase-change memory applications, PDR switching in GST-based materials was only recently discovered.[26,27] The material under study consisted of $Ge_2Sb_{2+x}Te_5$, thus having excess Sb with respect to the stoichiometric composition $Ge_2Sb_2Te_5$. Despite the lack of direct evidence, PDR switching was attributed to the formation and rupture of Sb filaments (bridges) upon alternating the direction of the applied voltage/current. In order to confirm this mechanism, it has to be shown that the excess Sb present in $Ge_2Sb_{2+x}Te_5$ plays a crucial role. For this purpose, we compare the switching properties of stoichiometric $Ge_2Sb_2Te_5$ films with those of Sb-excess $Ge_2Sb_{2+x}Te_5$ films.

The specimens investigated consist of GST(40 nm)/Mo(100 nm) films deposited in a single run without breaking the vacuum by dc magnetron sputtering on silicon substrates. The GST layer is either stoichiometric $Ge_2Sb_2Te_5$ or Sb-excess $Ge_2Sb_{2+x}Te_5$ ($0.25<x<0.3$). Figure 1(a) shows schematically the structure of the capacitorlike memory cells with top electrodes of Ag with size ~1 mm^2 or Al of size ~0.003 mm^2. Al top-electrode pads were fabricated by sputtering with shadow mask. A thin gold wire was then ultra-

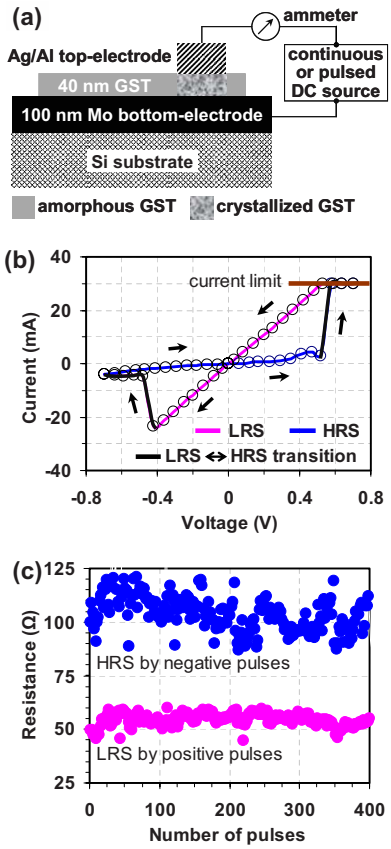

FIG. 1. (Color online) (a) Schematic (not to scale) of a capacitorlike memory cell with Ag/Al top-electrode, GST active layer and Mo bottom-electrode. (b) *I-V* characteristic of such a cell with $Ge_2Sb_{2+x}Te_5$ layer and Ag top-electrode showing PDR switching behavior. (c) Pulse-mode operation of the cell with voltage pulses of ±1.0 V amplitude and 250 μs width.

a)Electronic mail: b.j.kooi@rug.nl.

sonically soldered with the pads. In the case of fabricating Ag top-electrodes, thin Au wires were bonded with Ag-epoxy conductive adhesive onto the phase-change layer. Furthermore, prior to PDR switching the volume of GST film underneath the top-electrode was electrically crystallized by Joule heating due to electron conduction across the film. As a result, the initial (virgin) resistance of the cell is considerably reduced to lower values.

After the initial crystallization, PDR switching characteristics were investigated via *I-V* measurements using a Keithley 2601 sourcemeter with a voltage sweep rate of ~0.8 V/s. Voltage pulses of amplitudes above a certain threshold voltage (V_{th}) with positive and negative polarity were used to switch the cell resistance between low and high levels, respectively. Positive means the top electrode acts as anode and bottom electrode as cathode. In pulse-mode operation, a pulse generator (Stanford Research System Inc., Model DG535) capable of producing positive or negative voltage pulses of various amplitudes and widths was used. Before and after the switching, the cell resistance was read with low magnitude voltage pulses (0.1 V and 20 ms duration) of either polarity.

A typical *I-V* behavior of a cell with the Sb-excess GST film is shown in Fig. 1(b) with Ag as top electrode. Sweeping the voltage through negative values (with respect to the bottom grounded electrode), a linear *I-V* trend is observed up to −0.4 V, followed by a sudden change in cell resistance which is about 15 times higher than the previous one. The cell remains at this high-resistance state (HRS) up to −0.6 V and from −0.6 to +0.5 V. The HRS exhibits a linear *I-V* behavior in the voltage range −0.6 to +0.5 V. For $V>$ +0.5 V the cell switches back to its low-resistance state (LRS), where the current can rise to a limit of 30 mA, which is set in order to prevent any permanent electrical breakdown of the cell. The *I-V* characteristic in Fig. 1(b) exhibits the two metastable resistance states associated with PDR switching and reproduces the states for a number of cycles. Notably, the LRS and HRS were tested to be nonvolatile at room temperatures for a period of several months. In addition, as we proved in Ref. 26, the HRS during PDR switching is not related to switching to the (higher resistance) amorphous phase. Both HRS and LRS are associated with the phase-change material in-between the electrodes that is initially electrothermally crystallized.[26]

In order to allow high recording speeds and also to lower the electrothermal effects causing cell damage by continuous current flow, we examined PDR switching with dc voltage pulses. Switching pulses (of positive or negative polarity) were injected from the top-electrode while the bottom-electrode was grounded. Negative voltage pulses led the cell to HRS, whereas the positive pulses to LRS [see Fig. 1(c)]. The resistance state of the cell was measured using a read pulse (0.1 V, 20 ms) of either polarity having a much lower voltage than the switching pulses.

Compared to switching with continuous dc voltages [Fig. 1(b)], the threshold voltage for switching in pulse-mode is higher but the cyclability is significantly improved. For example, in Fig. 1(c) the switching (with voltage pulses of 1.0 V and 250 μs) is demonstrated for at least 400 cycles with HRS-LRS contrast of ~150%. In many experiments with Ag top-electrodes, the cell resistance switched between

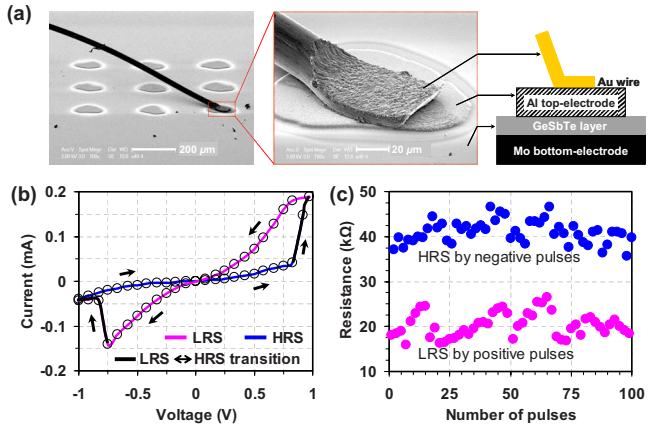

FIG. 2. (Color online) (a) Scanning electron microscope image (left) showing an array of Al top-electrode pads on GST layer. The magnified image (middle) shows a thin Au-wire ultrasonically bonded to one of the pads. Image on the right-side shows the schematic drawing of the cell. (b) *I-V* characteristic of such a cell with $Ge_2Sb_{2+x}Te_5$ layer and Al top-electrode showing the typical switching behavior. (c) Pulse-mode PDR switching of the cell with voltage pulses of ±1.5 V and 250 μs.

~50 and 100 Ω and the cell resistivities were measured to be ~1 and 2 kΩ m, respectively.

Furthermore, cells with Al top-electrodes were used to investigate switching at micron scales [Fig. 2(a)]. A typical *I-V* characteristic demonstrating PDR switching of this cell type is shown in Fig. 2(b). Switching from HRS to LRS and LRS to HRS occurred at about +0.8 and −0.75 V, respectively. In contrast to the cells with Ag top-electrodes, the LRS now deviates from Ohmic behavior. Although the reason for the deviation is not fully understood, it is expected to be related with a Schottky-type barrier formation at the top-electrode/GST interface. The interface properties (varying with the electrode material type) could influence the barrier properties. The pulse-mode operation of the cell with 1.5 V and 250 μs pulses is shown in Fig. 2(c). The switching between the two resistance states (LRS of ~20 kΩ and HRS of ~40 kΩ) with a resistance contrast of ~100% was stable for more than 100 cycles. The cell resistivity values at LRS and HRS with Al top-electrode were comparable to those of the cell with Ag top-electrode (i.e., ~1 kΩ m at LRS and ~2 kΩ m at HRS).

The present results from capacitorlike cells and those with conductive-AFM (C-AFM) (Refs. 26 and 27) indicate that PDR switching does not depend critically on the electrode material. The resistance contrast between LRS and HRS measured by C-AFM was as high as three orders of magnitude,[26,27] and thus much higher than that measured with the capacitorlike cells. The LRS resistivity of cells formed with the C-AFM is comparable with that of the capacitorlike cells. However, the HRS resistivity for the cells formed with C-AFM was much higher than that of the capacitorlike cells. Indeed, large-sized electrodes can in general be associated with a kind of local short-circuits (leakage flows) leading to loss of the resistance contrast due to a lower HRS. The existence of PDR switching irrespective of the electrode material type indicates that the switching is an intrinsic property of the $Ge_2Sb_{2+x}Te_5$ film. A detailed mechanism based on formation and rupture of conductive Sb-filaments bridging the crystallites and both electrodes was suggested in Ref. 26.

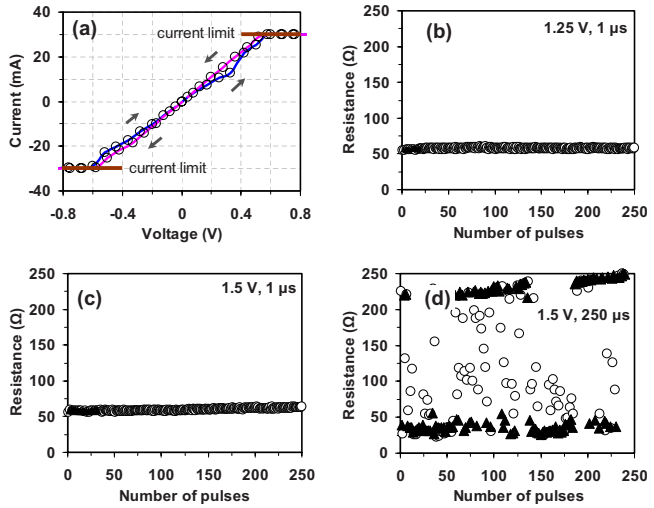

FIG. 3. (Color online) (a) *I-V* characteristic of a capacitorlike cell, containing stoichiometric $Ge_2Sb_2Te_5$ film and Ag top-electrode, showing the absence of PDR switching behavior. (b) Variation in cell resistance for 1.25 V and 1 μs pulses, (c) variation in cell resistance for 1.5 V and 1 μs pulses, and (d) variation in cell-resistance for 1.5 V and 250 μs pulses. ▲: positive pulses; O: negative pulses. Important to note that the results shown in [(b)–(d)] are examples of consecutive tests performed on a single cell, such that finally the cell in (d) can show variations in resistance due to the extensive electrothermal stresses imposed to the cell.

In order to reveal the importance of excess-Sb in PDR switching, capacitorlike cells with stoichiometric $Ge_2Sb_2Te_5$ films (where Sb-bridging is not likely) and Ag top-electrodes were investigated. Structure and dimension of the cells were similar to the one shown in Fig. 1(a). Similarly with the Sb-excess GST film, the volume underneath the top-electrode was electrically crystallized with a continuous-dc voltage prior to PDR switching experiments. An *I-V* characteristic is shown in Fig. 3(a) and it does not show any resistance switching. The cell current increases linearly with the applied voltage in both positive and negative directions, meaning that the cell resistance is independent of the voltage polarity. In contrast to the previous observation with the Sb-excess GST specimen, the threshold-point in the applied voltage supposed to appear at ~0.5 V is not detected [comparing Figs. 1(b) and 3(a)], i.e., the cell remains in one single resistance state (LRS) and fails to show PDR switching.

Moreover, pulse-mode PDR switching was examined with dc voltage pulses of various amplitudes ($\geq$1 V) and widths ($\geq$1 μs) as it is shown in Figs. 3(b) and 3(c). Application of the switching pulses (sufficiently long to trigger if possible switching) with positive and negative polarity from the top-electrode for more than 100 cycles did not result in any PDR switching. The cell remained in a single resistance state as it responded previously for the continuous dc voltages [cf. Fig. 3(a)]. Prolonged and repetitive application of the voltage pulses across a single cell eventually leads to fluctuations in the cell resistance, as shown in Fig. 3(d), due to the possible electrothermal effects including damage/degradation like segregation or phase-separation[28] of the GST layer.

In conclusion, PDR switching experiments with stoichiometric $Ge_2Sb_2Te_5$ films, as compared to those with Sb-excess $Ge_2Sb_{2+x}Te_5$ films, prove that the excess Sb-content in the films is crucial for PDR switching. Therefore, the switching between LRS and HRS can be attributed to the formation and rupture of electrically conductive Sb-bridges between the $Ge_2Sb_2Te_5$ nanocrystals and the electrodes through a resistive amorphous phase. The coexistence of the two types of resistance switching mechanisms, i.e., phase-change and polarity-dependent, in a single dedicated phase-change material can expand the applicability of GST films in future data storage systems.

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